Aerospace Research Center

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LIQUID LASER PARAMETERS

Semi-Annual Technical Report
Contract Nonr-4644(00)
August 1, 1966 – January 31, 1967

Prepared for the

Scientific Officer
Physical Sciences Division
Office of Naval Research
Washington 25, D.C.

by

David L. Williams
Daniel Grafstein
Aryeh H. Samuel

27 February 1967

RESEARCH CENTER
GENERAL PRECISION
AEROSPACE GROUP
LITTLE FALLS, NEW JERSEY

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Dr. Daniel Grafstein,
Principal Staff Scientist
Manager, Materials Department.

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FOREWORD

This is the Semiannual Technical Report on liquid laser parameters which covers research done under Contract NONR 4644(00) between the Office of Naval Research and the General Precision Aerospace Research, Little Falls, New Jersey. This report covers research performed during the period 1 August 1966 to 31 January 1967.

The authors of this report are Drs. D. L. Williams, D. Grafstein, and A. H. Samuel. Dr. Irving Rowe of the Office of Naval Research, New York, has acted as Project Scientist. The authors are indebted to Mr. C. Whitmore for experimental assistance, and Dr. N. Blumenthal for many helpful discussions.

ABSTRACT

Contract Nonr - 4644(00)

Attempts have been made to extend the calculation of energy-flow diagrams to a series of additional europium(III) complexes. This has led to the appearance of negative rate constants, a physically impossible result. The equations and assumptions which describe the system are reviewed, and a possible improved approach is described.

It has been ascertained that previous assumptions could be eliminated if one additional variable could be measured. A prime possibility is the steady-state population of the emitting level. A feasible manner of measuring such a quantity appears to be electron paramagnetic resonance.

A recalibration of the fluorescence-measuring apparatus has been performed, and several modifications introduced which have increased the accuracy of the measurements.

Fluorescent spectra of a number of terbium(III) complexes have been obtained. These data reveal that for terbium, as for europium, the alkyl phosphate complexes are the most promising for laser applications.

I. INTRODUCTION

This is the fifth semiannual report on an investigation of the factors influencing the fluorescence of rare-earth ions. One important aim of this work is to produce a system capable of efficient lasing based on the direct excitation of rare-earth ions in solution. Most of the work has dealt with the characteristics of europium(III) in various chemical environments in an attempt to understand the effects of environment on fluorescence, and thereby learn how to optimize lasing potential.

The europium(III) system can be described in terms of six transitions, three radiative and three nonradiative. A general energy-level diagram is presented in Figure 1. The energy levels have been numbered sequentially from one for the ground level to five for the excited level, and will be referred to by these numbers. The actual term symbols are also given on the Figure. Level 5 is representative of any one of the several intermediate levels to which the europium may be excited.

The intensity of a transition between levels i and j, either radiative or nonradiative, is designated Q_{ij} and is given in quanta/second. To completely characterize the system it is necessary to know the value of all Q's. The intensities of the radiative transitions, Q_{15}, Q_{42}, and Q_{43}, are all obtainable experimentally.

The ratio of Q_{42} to Q_{43} is proportional to the ratio of the areas of the fluorescent peaks, and the proportionality constant is obtainable from the correction curve for the spectral response of the phototube.

$$\frac{Q_{42}}{Q_{43}} \quad C \frac{A_{42}}{A_{43}} \tag{1}$$

The total quantum efficiency is the number of quanta emitted per quantum absorbed, and can be written

$$\epsilon = \frac{Q_{42} + Q_{43}}{Q_{15}} \tag{2}$$
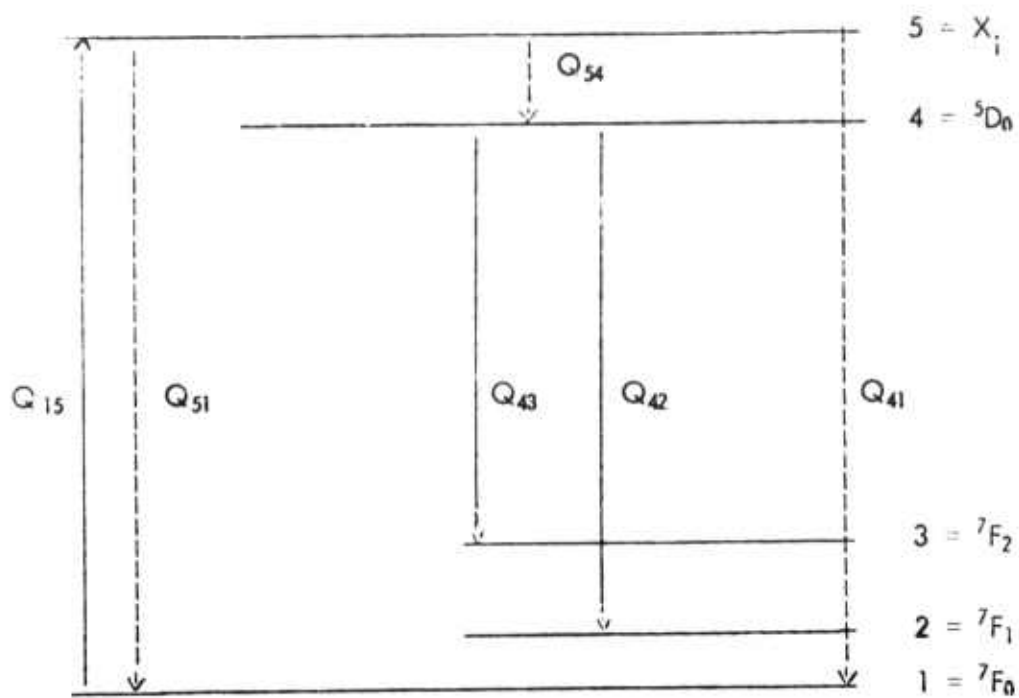
ENERGY LEVEL DIAGRAM FOR Eu(III)

FIGURE I

The value of ϵ can be determined by comparison with a standard of known quantum efficiency. The substance Rhodamine B has been used in this program for this purpose.

Measurement of the absolute number of photons being absorbed by the sample will yield Q_{15}. This has not been done thus far in the program. There are several experimental techniques available to accomplish this including the use of an actinometer or a calibrated thermopile. Such a thermopile is available in this laboratory.

The above three parameters (C, ϵ, Q_{15}) allow one to compare the relative efficiencies of a series of europium(III) complexes as regards their possible potential for lasing action. However, they reveal nothing about the nonradiative transitions which have a decided effect on exactly how large a population inversion is achieved. In order to maximize the laser action by altering the chemical environment of the europium, one must know how these nonradiative transitions are influenced by the ligand.

It is possible to write two additional relationships:

$$Q_{15} = Q_{51} + Q_{54} \tag{3}$$

$$Q_{54} = Q_{41} + Q_{42} + Q_{43} \tag{4}$$

There is still one less relationship than the number of unknowns. The flow diagrams given in the last quarterly and last semiannual reports were obtained with the assumptions that for $EuCl_3$ in triethylphosphate (TEP) the rate of the $4 \rightarrow 1$ transition was zero and that for other compounds the rate of the $4 \rightarrow 2$ transition was identical to its rate in $EuCl_3$ in TEP. These assumptions were based on the apparent constancy of τ_{42}.

$$\tau_{42} = \frac{1}{K_{42}} = \tau \left(1 + \frac{k_{43}}{k_{42}}\right) \tag{5}$$

where τ is the decay time for level 4, τ_{42} is the hypothetical decay time for the $4 \rightarrow 2$ transition, and the k's are rate constants for the respective transitions. This equation was

derived in the last semiannual (February 1, 1965 – July 31, 1966), and for five complexes τ_{42} was constant to $\pm 2\%$.

The rates can be related to the respective rate constants by

$$Q_{ij} = k_{ij} [N_i] \qquad (6)$$

where N_i is the steady-state population of level i.

II. ENERGY FLOW DIAGRAMS

In the eighth quarterly report, a complete energy-flow diagram was given for the triethyl-phosphate complex of europium nitrate. It was next desired to obtain similar diagrams for the other complexes whose fluorescence has been observed. This was easily accomplished for the europium chloride-triethylphosphate complex, and the diagram was included in the last semiannual. It then became desirable to attempt to delineate the characteristics of the other complexes, these being

europium nitrate – dimethyl sulfoxide,	$Eu(NO_3)_3 \cdot x \ (CH_3)_2 \ SO$	(Eu-N-DMSO)
europium chloride – dimethyl sulfoxide,	$EuCl_3 \cdot x \ (CH_3)_2 \ SO$	(Eu-Cl-DMSO)
europium nitrate – dimethyl acetamide,	$Eu(NO_3)_3 \cdot x \ CH_3CON(CH_3)_2$	(Eu-N-DMAC)
europium chloride – dimethyl acetamide,	$EuCl_3 \cdot x \ CH_3CON(CH_3)_2$	(Eu-Cl-DMAC)
europium nitrate – dimethyl formamide,	$Eu(NO_3)_3 \cdot x \ HCON \ (CH_3)_2$	(Eu-N-DMF)
europium chloride – dimethyl formamide,	$EuCl_3 \cdot x \ HCON \ (CH_3)_2$	(Eu-Cl-DMF)

(The abbreviations in parentheses will be used henceforth.

The areas under the fluorescent peaks were measured for these six complexes, and the following values of k_{42}/k_{43} (from (5), $k_{43}/k_{42} = Q_{43}/Q_{42}$) were obtained:

	Eu-N-DMSO	Eu-Cl-DMSO	Eu-N-DMAC	Eu-Cl-DMAC	Eu-N-DMF	Eu-Cl-DMF
$k_{43}/k_{42} =$	1.49	1.78	4.71	3.84	4.23	4.48

The lifetime studies reported in the last semiannual allow a determination of τ, the decay time for level 4. This is related to the rate constants by

$$1/\tau = k_{41} + k_{42} + k_{43} \qquad (7)$$

The quantity k_{42} was postulated as being independent or nearly independent of chemical environment and has been measured as $109 \ sec^{-1}$ for the triethylphosphate complex of europium nitrate, $Eu(NO_3)_3 \cdot 3(C_2H_5O)_3 \ PO$ (Eu-N-TEP).

An attempt was made during the eighth quarter to obtain k_{42} values for the other complexes from the absorption intensities of the reverse transition $^7F_1 \longrightarrow {}^5D_0$. There is a considerable absolute discrepancy. However, if the relative values are taken to be reliable, and the value of 109 sec^{-1} for Eu-N-TEP is accepted, values ranging from 98.2 to 193.7 sec^{-1} for the other complexes are obtained. Using these absorption-corrected values of k_{42} and the measured values for τ, Table I was obtained.

For the two dimethylacetamide complexes, the calculations yield negative values for k_{41}, the rate constant for nonradiative decay from the emitting level. Since negative rate constants are physically impossible, there must be an error. Simply a change in the assumptions made could correct the situation; conversely, an error in the data could be the source of difficulty.

The reliability of the data is dependent upon the accuracy of the instrumental measurements. While there is no specific indication that any of the previously obtained data is erroneous, it was deemed prudent to check the calibration of the instruments.

TABLE I

Complex	$\tau\,(x\,10^{-3})$	k_{42}	k_{43}	k_{41}
Eu-N-DMSO	1.46	187	279	218
Eu-Cl-DMSO	1.20	193	345	295
Eu-N-DMAC	1.94	152	716	-253
Eu-Cl-DMAC	1.46	158	608	-83
Eu-N-DMF	1.13	129	546	172
Eu-Cl-DMF	0.93	140	625	310
Eu-N-TEP	1.92	109	367	46
Eu-Cl-TEP	1.45	98	591	0
Eu-Cl-H2O	0.12	123	15	8200

$k_{41} = (1/\tau) - k_{42} - k_{43}$;

Eu-N-TEP is the europium nitrate-triethylphosphate complex
$Eu(NO_3)_3 \cdot 3(C_2H_5O)_3PO$;
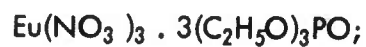
Eu-Cl-TEP is the europium chloride-triethylphosphate complex
$EuCl_3 \cdot 3(C_2H_5O)_3PO$;
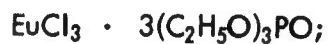
Eu-Cl-H2O is the europium chloride-water complex $[Eu(H_2O)_6]Cl_3$

III. IMPROVEMENT OF EXPERIMENTAL TECHNIQUES

1. Instrument Recalibration

The Aminco-Bowman Spectrophotofluorometer was recalibrated as to the accuracy of the emission monochromator and the spectral response of the phototube. The monochromator was calibrated with a high-pressure mercury-discharge lamp and a sodium lamp. All emission lines were easily identified and a linear correction established for the wavelength readings. The spectral response of the phototube was determined by illuminating the sample cavity with a tungsten source which closely approximates black-body radiation. Comparison of the output with a standard black-body spectral curve yielded the correction curve. The previous correction factor reported for the area of the $4 \to 3$ transition was 2.82. The re-calibration now yields a somewhat larger number of 4.39. It must be noted, however, that this does not affect the negative aspect of the k_{41} values, though it will alter the absolute magnitude.

2. Lifetime Measurements

In order to increase the accuracy of lifetime measurements, certain modifications are being made in the instrumental set-up. Previous measurements have had an error confidence of $\pm 10\%$. The arrangement is to be the same as described in the last semiannual (p. 11) but instead of a constant chopper with variable speed, a constant-speed motor will be used with a set of accurately machined choppers. The constant-speed motor will give greater repro-ducibility of the data. A more precise monochromator has been made available than was used previously.

3. Fluorescent Measurements

It has been determined that a large increase in slit width on the excitation side of the spectrophotofluorometer does not alter the general characteristics of the fluorescent output. It does, however, allow more excitation light to fall on the sample with a corresponding increase in signal intensity. The noise level remains approximately constant and thus the large output allows a more precise determination of intensity. It has also been possible

to decrease the scanning speed of the emission monochromator; this also increases the area of the recorded spectra, again allowing a more precise measurement. It is estimated that the precision has been increased by a factor of five by using these new techniques.

IV. ALTERNATE METHOD OF ENERGY DIAGRAM GENERATION

If one does not make the assumptions discussed previously, it is necessary to make some other experimental determination in order to completely characterize the system. Equation (6) relates the fluorescent intensities to the rate constants, and Equation (7) relates the experimental decay time to the rate constants. Thus, if N_4, the steady-state population of the emitting level, could be measured, this would provide the necessary additional measurement.

Europium(III) is a paramagnetic ion in all levels and is thus susceptible to investigation by electron paramagnetic resonance (EPR). The intensity of an EPR signal is proportional to the number of ions in the level in which resonance is occurring. In principle, measuring the intensity of the EPR signal arising from level 4 while the sample is being illuminated will give a measurement indicative of the steady-state population provided we can distinguish the signals from various levels. An absolute number can be obtained by comparison of this signal with a standard having a known population. The most feasible standard would be the ground level of the same sample when unilluminated.

V. FLUORESCENT INTENSITIES OF TERBIUM COMPLEXES

A number of fluorescent spectra of terbium complexes have been taken. Table II shows the uncorrected relative intensities of the fluorescent lines at 487, 548, 587 and 625 nm. The correction factors are expected to be small, at least for the first three lines, but are not available at this time. The peaks areas (height x full width at half height) are normalized on the 487 nm line. The fluorescent line $^5D_4 \rightarrow ^7F_3$ (625 nm) is quite weak, and the few values given were obtained from spectra run at greater sensitivity in which only the 625 nm and 586 nm lines were measured. These should be considered as "order of magnitude" values.

The relative intensities given in Table II show that the hypothesis brought forward in the last semi-annual report, viz, that the relative transition probabilities for the terbium fluorescent lines do not vary with environment, is only a first approximation. It does appear to hold, within the limits of experimental error, for the complexes with alkyl phosphates and substituted amides. The aqueous terbium ion shows a relatively stronger transition at 587 nm and a weaker transition at 548 nm. The dimethylsulfoxide complexes are intermediate between the aquo and the other complexes.

If we now consider the implications of these data for a potential terbium liquid laser, we can draw the following tentative conclusions:

1. The most promising laser transition is $^5D_4 \rightarrow ^7F_5$ which is the most intense in all cases. The terminal state is about 2300 cm^{-1} above ground level so that this can be a four-state laser to good approximation.

2. The most promising complex would be one which combines high relative intensity of this line with long fluorescent lifetime (minimal non-radiative relaxation). The phosphate and amide complexes are superior in the first particular, the phosphate and sulfoxide complexes in the second (see Semi-Annual Report, Table IV, p. 31). It therefore appears that for terbium, as for europium, the alkyl phosphate complexes are most promising for laser applications.

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TABLE II

RELATIVE FLUORESCENCE INTENSITIES OF TERBIUM LINES *

Complex	$^5D_4 \longrightarrow {}^7F_3$ (625 nm)	$^5D_4 \longrightarrow {}^7F_4$ (587 nm)	$^5D_4 \longrightarrow {}^7F_5$ (548 nm)
Tb-N-DMSO		0.25	2.06
		0.23	1.57
		0.27	1.60
		0.18	1.34
		0.23 Ave.	1.67 Ave.
Tb-Cl-DMSO		0.25	1.98
Tb-N-DMAC	0.019	0.19	2.22
		0.16	2.16
		0.14	2.05
		0.13	1.27
	0.02	0.15 Ave.	1.93 Ave.
Tb-Cl-DMAC		0.13	2.16
Tb-N-DMF		0.18	2.24
		0.17	2.00
		0.18	1.99
		0.18 Ave.	2.08 Ave.
Tb-Cl-DMF	0.012	0.18	2.70
Tb-N-TEP	0.007	0.16	2.27
		0.15	2.18
		0.16	2.12
		0.15	1.90
	0.01	0.16 Ave.	2.12 Ave.
Tb-N-TBP		0.17	2.16
		0.15	1.93
		0.16 Ave.	2.05 Ave.
Tb-N-H$_2$O		0.22	1.49
		0.20	1.41
		0.28	1.29
		0.23	1.63
		0.23 Ave.	1.45 Ave.

* The intensity of the $^5D_4 \longrightarrow {}^7F_6$ line (487 nm) is taken as unity; it is therefore not listed.

VI. OTHER SOLVENT SYSTEMS

1. Nitrate Salts

The success of another laboratory in producing a liquid laser in an inorganic medium has caused us to think about possible inorganic media which would allow efficient rare-earth fluorescence but would not be as corrosive, poisonous, and unstable as selenium oxychloride. Anhydrous ionic melts appear to fulfill these conditions. Their disadvantage is that they require an elevated temperature to be liquid. We have therefore investigated the possibility of lowering the melting point.

A literature study showed that the melting points of pure alkali nitrates vary from 251° C (lithium) to 414° C (cesium). Eutectic mixtures have lower melting points. A mixture of $NaNO_3$ (11.8 mole %), KNO_3 (39.4), $Ca(NO_3)_2$ (48.8) is reported to melt at 133° C and a mixture of $NaNO_3$ (29.5 mole %), $LiNO_3$ (14.5), and $Cd(NO_3)_2$ (56.0) is reported to melt at 110° C. Lower melting points are reported for mixtures containing silver, e.g. 76° for $AgNO_3$ (52 mole %), $TlNO_3$ (45.8), $NaNO_3$ (1.7), KNO_3 (0.5). However, the photosensitivity of the silver ion makes its use undesirable.

We have prepared the sodium-potassium-calcium nitrate eutectic and confirmed that it is liquid at 133° C. Upon cooling, a supercooled syrup is formed, which hardens into a glass on further cooling. On one occasion, crystalization was observed.

The calcium nitrate used was the tetrahydrate. The melt was heated in an ethylene glycol bath at 160° C for about two hours and the weight was monitored. The heating was not sufficient to remove all the water. Since our studies have shown that in general traces of H_2O can greatly reduce fluorescence, it would seem desirable to prepare the melts from anhydrous dried salts.

Preliminary experiments demonstrated that europium and terbium nitrates were soluble in these melts. No visible enhancement of fluorescence was seen, but this is not considered significant in view of the presence of water.

2. inorganic Liquids

The concept developed here regarding the process controlling nonradiative transitions relates the magnitude of the transition to a multiple of ν_{vib}, the vibrational energy of the ligand bonds adjacent to the europium ion. Consequently, there should be an optimum value of ν_{vib} for every system. Such an optimum value should be determinable empirically for the europium(III) system by systematically altering the ligand environment in order to obtain a series of ν_{vib} values. A list of some suitable complexing solvent systems along with the maximum ν_{vib} for each is given in Table III.

Most of the compounds listed are toxic, and also react vigorously with water. In order to handle these chemical effectively, an inert atmosphere compartment has been obtained and installed.

TABLE III

Ligand	Maximum ν_{vib} in cm^{-1}
Br_3P	400
Cl_3P	511
Br_3SP	718
Cl_3SP	753
Cl_2SeO	955
Cl_2SO	1230
Cl_3PO	1285
Cl_2SO_2	1410
$Cl_2C_2O_2$	1800
SCN	2200

VII. <u>FUTURE PLANS</u>

1. A thorough study will be undertaken to establish the feasibility of measuring the steady-state population of level 4 by electron paramagnetic resonance, and the experiments carried out.

2. The instrumentation for lifetime studies will be set up and calibrated. Lifetime measurements will be made.

3. Work will be conducted on measuring the fluorescence of europium in a series of in-organic solvent systems with the objective of establishing an empirical relationship between the maximum ν_{vib} of the ligand and the laser potential of the europium.

4. The techniques developed for these europium systems will be utilized for the study of the laser potential of other rare-earth ions, particularly the terbium salts mentioned in this report.

5. Experiments on fluorescent rare-earth ions in anhydrous nitrate melts will be continued.

6. New concepts for potential liquid laser systems such as the terbium-phosphate system, will be evaluated.